53

X-RAY STUDY OF A DEHYDRATED PHASE OF COPPER AMMONIUM SULPHATE HEXAHYDRATE

GOURI BHOWMIK

MAGNETISM DEPARTMENT, I.A.C.S., CALCUTTA-32

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Plate X

ABSTRACT. The cell-dimensions of Cu $[(NH_4SO_4)]_2$ $6H_2O$ (monoclinic, space-group $P2_1/a$) as determined from rotation photograph are found to be $a = 9.27$Å, $b = 12.50$Å, $c = 6.33$Å $\beta = 106°5'$, with 2 molecules per unit cell. The results have been utilised to index the powder pattern of the substance. Analysis of the powder pattern by Lipson's method of the first stage dehydration product, $Cu[NH_4(SO_4)]_2$ $2H_2O$ formed at 65°C shows that the product has orthorhombic structure, the cell dimensions being $a = 14.84$Å, $b = 12.52$Å $c = 10.69$Å. The probable space groups are $Pmn\,2_1$ and $Pmnm$ with 8 molecules per unit cell.

INTRODUCTION

Magnetic measurements of the single crystals of a large number of Tutton salts (general formula $M(R\,X\,Y_4)_2$ $6H_2O$ where M = Mg, Zn, Cd, Cu, Ni, Co, Fe, etc. R = K, Rb, Cs, NH_4, $XY_4 = SO_4$, SeO_4 or BeF_4) showed (Bose *et al.* 1957 and 58) that they lose their magnetic anisotropies in the range 338°- 393°K the exact temperature depending upon the particular salt. This is evidently due to changes in crystal structure accompanying loss of water of crystallisation which causes the single crystals to become polycrystalline. Since the crystalline magnetic properties are intimately connected with the structure it would be interesting to study these changes in structure in order to elucidate the changes in the magnetic properties. As a typical case, the thermal dehydration of $Cu[(NH_4)SO_4]_2 6H_2O$ was undertaken and the corresponding changes in crystal structure investigated.

2. X-RAY MEASUREMENTS ON $Cu(NH_4SO_4)_2 6H_2O$

X-ray data on single crystls of Cu $[(NH_4)SO_4]_2$ $6H_2O$ is lacking, though one of the isomorphous salts $Mg[(NH_4)SO_4]_2 6H_2O$ has been studied using trial and error method by Hofmann (1931). By analogy with the latter it follows that $Cu[(NH_4)SO_4]_2$ $6H_2O$ is also monoclinic having 2 molecules in the unit cell and belongs to

the space-group $P2_1/a$. We have determined the dimensions of the unit cell from rotation photographs about the three crystallographic axes. They are

$$a = 9{\cdot}27\,\text{Å}$$
$$b = 12{\cdot}50\,\text{Å}$$
$$c = 6{\cdot}33\,\text{Å}$$
$$\beta = 106°5'.$$

The monoclinic angle β is found from the zero layer-line of the rotation photograph about b-axis.

A powder diffraction pattern has also been taken at room-temperature and the spacings indexed with the help of the above values of cell dimensions.

TABLE 1

dÅ	Intensity	$1/d^2$ observed	$1/d^2$ calculated	Indices
7.193	vw	0.0193	0.0190	110
6.105	ms	0.0268	0.0270	001
5.456	ms	0.0336	0.0334	011
5.129	w	0.0380	0.0384	120
4.418	w	0.0502	9.0504	200
4.188	vs	0.0570	0.0568	210
3.759	vs	0.0708	0.0702	130
3.620	w	0.0763	0.0758	220
3.386	ms	0.0872	0.0870	$13\bar{1}$
3.061	s	0.1067	0.1066	112
2.486	s	0.1235	0.1239	212
2.715	w	0.1357	0.1353	321
2.556	m	0.1531	0.1528	240
2.441	s	0.1678	0.1673	$33\bar{1}$
2.229	ms	0.2013	0.2017	400
2.176	w	0.2112	0.2104	042
			0.2104	250
2.144	w	0.2175	0.2170	$25\bar{1}$
2.097	ms	0.2274	0.2273	420
2.031	w	0.2424	0.2431	003
1.963	w	0.2595	0.2593	430
1.922	ms	0.2707	0.2712	$31\bar{3}$
1.858	w	0.2897	0.2897	233
			0.2893	312
1.816	w	0.3032	0.3040	440
1.768	w	0.3200	0.3206	510
1.736	w	0.3318	0.3312	351
1.701	w	0.3456	0.3454	043

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PLATE X

(a)

(b)

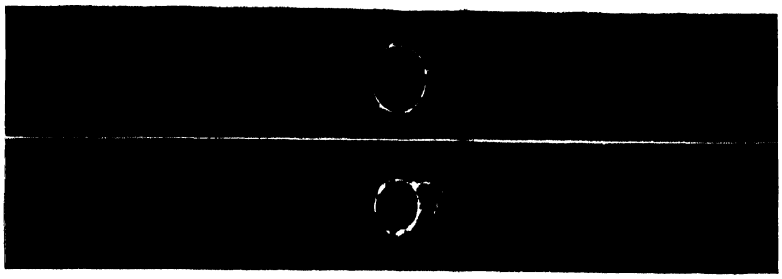

Fig. 1. Debye-Scherrer patterns

(a) Copper ammonium sulphate hexahydrate $Cu[(NH_4)SO_4]_2\,6H_2O$

(b) Copper ammonium sulphate dihydrate $Cu[(NH_4)SO_4]_2\,2H_2O$

The conditions of reflection satisfied are :

$h\,k\,l$: no condition

$h\,o\,l$: $h = 2n$.

There is no powder-line with *0k0* reflection. But rotation photographs show that for *0k0*, $k = 2n$ spots are present. Hence the space-group is P $2_1/a$ which supports the earlier assumptions.

STUDIES ON THE DEHYDRATION PRODUCT

Next powdered sample of $Cu[(NH_4)SO_4]_2 6H_2O$ of weighed quantity is heated automatically controlled thermostatic oven and the loss of weight at different temperatures is determined. At 338°K it shows an abrupt loss of weight which corresponds to 4 molecules of water. When the temperature is brought down the sample soon regains its original weight. It indicates that $Cu[(NH_4)SO_4]_2 6H_2O$ undergoes a reversible transformation to a dihydrate at 65°C. This is also evident from the X-ray powder pictures.

It is interesting to study the structure of the dehydrated product. Since the dehydrated powder absorbs moisture rather quickly, instead of packing the dehydrated powder in capillary tubes in the usual way, the capillary tube is first packed with finely powdered $Cu[(NH_4)SO_4]_2 6H_2O$, now the fine tube packed and open at both ends is heated in the oven at a constant temperature somewhat above 65°C for 24 hours when it attains constant weight.

The capillary tube is now quickly sealed at both ends so that the treated sample does not come in contact with moisture from the atmsophere. The sample is mounted in a camera of 57.3 mm radius and X-ray powder photograph is taken with CuK_α radiation from a Raymax 60 Diffraction unit running at 50KV and 10 mA. The powder pattern thus obtained is entirely different from that for $Cu[(NH_4)SO_4]_2 6H_2O$. Besides, the spacings measured for the powder-line has no spacing common with the known spacings of either of $(NH_4)SO_4$ or $CuSO_4$ (anhydrous) or $CuSO_4H_2O$. This shows that the dehydrated product is a new double salt having a unique crystal structure. If the dehydrated powder is cooled to room-temperature in contact with atmosphere and photograph taken, the orignal powder pattern of $Cu[(NH_4)SO_4]_2 6H_2O$ is obtained. The powder photograph is the only source of information regarding the structure of the new compound since, in spite of many attempts the substance could not be obtained as single crystals from aqueous medium. Hence attempt has been made to index the powder-photograph taking the substance to have the molecular formula $Cu[(NH_4)SO_4]_2 2H_2O$.

First attempts were made to index the powder lines in terms of cubic, tetragonal and hexagonal system. Since the data do not fit with either of these systems Lipson's method (Lipson, 1949) was applied to find if the crystal belongs to the

orthorhombic system. For orthorhombic system, $\sin^2\theta$ values obtained from each pair of Debye-Scherrer ring can be written as

$$\sin^2\theta_{hkl} = \frac{\lambda^2}{4a^2}h^2 + \frac{\lambda^2}{4b^2}k^2 + \frac{\lambda^2}{4c^2}l^2$$

$$= Ah^2 + Bk^2 + Cl^2 \quad \text{where} \quad A = \frac{\lambda^2}{4a^2} \quad B = \frac{\lambda^2}{4b^2} \quad C = \frac{\lambda^2}{4c^2}$$

TABLE II

dÅ	Intensity	$\sin^2\theta$ observed	$\sin^2\theta$ calculated	Indices
12.199	w	0.0039	0.0038	010
8.023	s	0.0092	0.0090	011
6.193	s	0.0155	0.0152	020
5.771	w	0.0178	0.0179	120
5.345	s	0.0209	0.0208	002
4.551	w	0.0287	0.0282	310
4.331	vs	0.0317	0.0312	221
4.312	vs	0.0319	0.0316	202
3.952	ms	0.0381	0.0387	122
3.785	ms	0.0415	0.0421	131
3.642	w	0.0448	0.0447	321
3.508	w	0.0483	0.0484	401
			0.0488	312
3.364	vw	0.0525	0.0522	411
3.268	vs	0.0557	0.0550	032
3.226	vs	0.0571	0.0577	132
3.150	m	0.0599	0.0603	311
3.064	vs	0.0631	0.0635	140
3.033	vs	0.0646	0.0640	402
			0.0647	132
2.960	w	0.0679	0.0678	412
2.885	w	0.0714	0.0713	510
2.447	ms	0.0788	0.0792	422
			0.0793	332
2.657	ms	0.0842	0.0843	142
2.514	w	0.0904	0.0898	114
2.495	w	0.0955	0.0950	050
2.450	s	0.0990	0.0984	024
2.298	w	0.1126	0.1124	610
2.139	s	0.1299	0.1302	414
2.081	s	0.1373	0.1368	060
			0.1365	115
1.983		0.1511	0.1508	443
1.922		0.1609	0.1611	360
1.762	ms	0.1915	0.1010	016
1.730	ms	0.1986	0.1983	741
1.521	w	0.2571	0.2575	107
1.497	w	0.2653	0.2661	715

The values of $\sin^2\theta_{hkl}$ known as q-values observed from the pattern are listed in Table II. With the above values of $\sin^2\theta$, the difference diagram is drawn according to Lipson's method. The diagram shows frequently-occurring values

from which the values of the constants A, B, C are determined in the following way.

If we choose the first three values of Δq from the Lipson's chart i.e., 0.0028, 0.0038, 0.0052, we find that (1) the 4 fold and 9 fold multiples of A i.e., .0110, .0250 are present,(2) the 4 fold, 9 fold, 16 fold multiples of B i.e., 0.0152, 0.0340, 0.061 are frequently occurring, (3) the 9 fold, 16 fold and 25 fold multiples of C i.e., 0.046, 0.083 and 0.1300 are also present in the chart.

There are no other value of Δq in the Lipson's chart which has so many multiples present. So these are the most probable values of constants A, B, C. With these values of A, B, C all the values of $\sin^2\theta_{hkl}$ in Table II can be successfully indexed. For better adjustment A is taken as 0.0027 and the agreement between the observed and calculated values is highly satisfactory, the discrepency lying within experimental errors. So it is concluded that the crystal belongs to the orhorhombic system, with the dimensions of the unit cell as calculated from A, B, C

$$a = 14.84\text{Å}$$
$$b = 12.52\text{Å}$$
$$c = 10.69\text{Å}.$$

Measurement of the density of the dihydrate is very difficult since it always tends to be converted into the hexahydrate when exposed to atmosphere. The hexahydrate powder is taken in a specially designed pyknometer and treated in the furnace at 70°C for about 24 hours so that the dihydrate is obtained. The pyknometer is cooled in a dessicator and weighed. Since the substance is highly soluble in water its density is measured with respect to paraffin oil of known density. Repeated measurements show that the density of the dihydrate is 2.04 gm/c.c.

With this value of density and the dimensions of the unit cell given above, the number of molecules per unit comes out as $7.50 \simeq 8$. The agreement is satisfactory in view of the fact that due to the extreme instability of the dihydrate, at room temperature, sufficient accuracy cannot be obtained in the determination of the density. This integral value also supports the choice of the unit cell of the crystal.

The conditions limiting possible reflections indicated by Table II are

hko : no condition
okl : no condition
hol : $h+l = 2n$
hko : no condition
hoo : $h = 2n$.
oko : no condition
ool : $l = 2n$,

The conditions agree with both the space groups $P_{mn}2_2$ and P_{mnm}. Since the substance has not yet been obtained in the single crystal form it is not possible to ascertain the space-group uniquely from single crystal photograph.

4. DISCUSSIONS

It is interesting to note that the orientation of the crystalline principal magnetic axes in the (010) plane of the crystal of $Cu[(NH_4SO_4)]_26H_2O$ changes by about 19° in the range 90°K to 338°K slowly at first and then rapidly as the transition temperature of 338°K is approached. Correspondingly the relative orientation between the approximate tetragonal axes of the two equivalent $Cu^{2+}6H_20$ octahedra equally inclined to the *b*-axis of the unit cell, change by about 10° (Bose *et al*, 1957). This indicates that even before the transition temperature is reached a rapid rearrangement of the constituents of the unit cell is taking place, owing to increased thermal motions, tending to make the four water molecules of coordination redundant for the stable equilibrium of the lattice at the transtion point, which becomes apparent by the fact that as soon as this temperature is reached these water molecules are thrown out of the lattice and the constituents of the unit cell assume the new symmetry of the orthorhmbic class for the dihydrate. The manner of reorientation by rotation of the $Cu^{2+}6H_2O$ groups about the *b*-axis previous to transition and the X-ray finding that the *b*-axial lengths of the hexahydrate and dihydrate are equal seem to indicate that there is a correspondance between the *b*-axes of the monoclinic and the orthorhombic varieties. Also the transition from monoclinism to orthorhombicity is attained at the transition temperature by a continuous approach of the *a* and *c* axes of the monoclinic cell towards orthogonality.

More X-ray data on the structure of the salt before and after transition would verify the predictions and attempts are being made to obtain these.

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